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Sampling and Analysis of Sediments in Dredged Material from Wilma Uplands Disposal Site

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Battelle/Marine Sciences Laboratory
Sequim, Washington

September 1992

Prepared for the U.S. Army Corps
of Engineers - Walla Walla District
under a Related Services Agreement
with the U.S. Department of Energy
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Pacific Northwest Laboratory
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SUMMARY

The Lower Granite Reservoir provides slack-water navigation for the Lewiston, Idaho, and Clarkston, Washington area. The levee system associated with the reservoir protects industrial, commercial, and residential areas from inundation of waters impounded behind the dam.

Sediment deposition at the confluence of the Snake and Clearwater rivers has required frequent dredging events in past years, including two recent events in 1986 and 1987. Dredging was necessary to maintain the depth of the navigation channel and the freeboard on the Lewiston Levee system.

Dredged material from the 1986 and 1987 events was placed in three containment ponds located on the north bank of the Snake River, near River Mile 134.7. The ponds were used to hold approximately 400,000 cubic yards of dredged material removed from the port areas at the confluence of the Snake and Clearwater rivers. The location of the three ponds is such that pond A drains into pond B, which drains into pond C. Pond C also contains a culvert designed to return excess water to the Snake River.

Prior to dredging, the river sediments were tested and found to be typical of non-contaminated sediment. Since that testing, dioxins and furans have been found in the effluent from a Kraft pulp mill in Lewiston that discharges directly into the confluence of the Snake and Clearwater rivers. Effluent and sludge samples taken in 1988 were found to contain concentrations of 71 to 79 parts per quadrillion (ppq) and 78 parts per trillion (pptr) of 2,3,7,8, tetrachloro dibenzo-p-dioxin (TCDD), which is the primary dioxin of concern. A small number of fish was also analyzed, the results of which showed levels of dioxins in their tissues were below the Food and Drug Administration standard of 25 pptr.

The U.S. Army Corps of Engineers (USACE) believed that dredged material placed in the containment ponds may contain contaminated levels of dioxins and furans. At their request, Battelle/Marine Sciences Laboratory (MSL) sampled sediments from these ponds and performed a chemical analysis.

A sampling scheme was developed by the USACE, Walla Walla District, and Waterways Experiment Station in Vicksburg, Mississippi, in conjunction with MSL personnel. A grid system was developed, consisting of 37 sampling stations. However, in the field, 2 additional samples

were taken at grid 16, which increased the total number of sampling stations to 39. Samples were collected in the center of each grid to the full depth of dredged material.

All 39 sediment samples were analyzed for total organic carbon (TOC), total volatile solids (TVS), and grain size. Only nine samples were analyzed for dioxins and furans, because dioxins and furans are insoluble and have a high affinity for organic material. Dioxin analysis included 2,3,7,8 TCDD at detection levels of 1 pptr and all other toxic dioxin/furan congeners to the lowest possible detection limit obtainable by Environmental Protection Agency (EPA) methods 8290. What follows is a summary of the chemical evaluations of grain size, TOC, TVS, and dioxins.

The majority of sediments contained fine silty material with particle sizes of 0.0039 to 0.0625 mm. Stations containing the finer-grained sediments also produced the higher levels of TOC, ranging from 0.17% to 3.55%. The association of fine-grained sediments with higher TOC levels may be attributed to the organic root material contained within the samples from those stations. Also, stations with the highest TOC levels had the highest TVS levels, ranging from 1.28% to 8.94%. Finally, the dioxin/furan results indicated that levels of 2,3,7,8 TCDD or TCDF were not detected in any of the nine samples. Chlorinated congeners of dioxins and furans were detected at some of the stations ranging from 0.15 pptr (12378-PeCDD) to 95 pptr (OCDD).

ACKNOWLEDGMENTS

The authors thank Nancy Kohn, Jeff Ward, and Rob Cuello for their efforts in making the field sampling a success. Many thanks to Rhonda Karls, Mike Barrows, Shannon Goodwin, and Nelson Topper for their diligent efforts in the laboratory. For the valuable assistance in the review of this document, we thank Dave Shreffler, Dick Ecker, Rob Cuello, and Wayne Gorst. Finally, a special thanks to Michele Finney without whom the preparation and publication of this report would not have been possible.

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1.0 INTRODUCTION

The Lower Granite Reservoir on the Snake River provides slack-water navigation for the Lewiston, Idaho, and Clarkston, Washington, area. The levee associated with this reservoir protects industrial, commercial, and residential lands from inundation by waters impounded behind the dam. To ensure the integrity of the navigation channel and the freeboard on the Lewiston levee system, the upstream portion of this reservoir was dredged in 1986 and 1987 to remove depositional sediment that had accumulated in the confluence of the Snake and Clearwater rivers.

To provide a disposal area for the dredged material, three containment ponds (A, B, and C), referred to as the Wilma Uplands disposal site, are located on the north bank of the Snake River at River Mile (RM) 134.7 (Figure 1.1). The three ponds were constructed so that Pond A drains into Pond B, which drains into Pond C. Pond C also contains a culvert designed to return excess water to the Snake River.

Prior to dredging and placement of dredged material in the containment ponds, the sediment was tested for a variety of contaminants. It was determined to be typical of non-contaminated sediments. In 1987, as a result of these tests, 400,000 cubic yards of material were placed in ponds A and B.

Since 1987, dioxins and furans were found in the effluent from a Kraft pulp mill, which discharges directly into the confluence of the Snake and Clearwater rivers. These chlorinated organic dioxins and furans are considered highly carcinogenic. Effluent and sludge samples taken in 1988 were found to contain concentrations of 71 to 79 parts per quadrillion (ppq) and 78 parts per trillion (pptr) of 2,3,7,8 tetrachloro dibenzo-p-dioxin (TCDD), which is the primary dioxin of concern. The tissues of fish native to the river were also tested. Results showed concentrations of dioxins in the tissues below the Food and Drug Administration standard of 25 pptr.

Because of concern that dredged material placed in ponds A and B may have contaminated levels of dioxins and furans, the U.S. Army Corps of Engineers (USACE) requested that Battelle/Marine Sciences Laboratory (MSL)[a] sample these sediments and perform chemical

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[a] The Marine Sciences Laboratory is part of the Pacific Northwest Laboratory, which is operated for the U.S. Department of Energy by Battelle Memorial Institute.

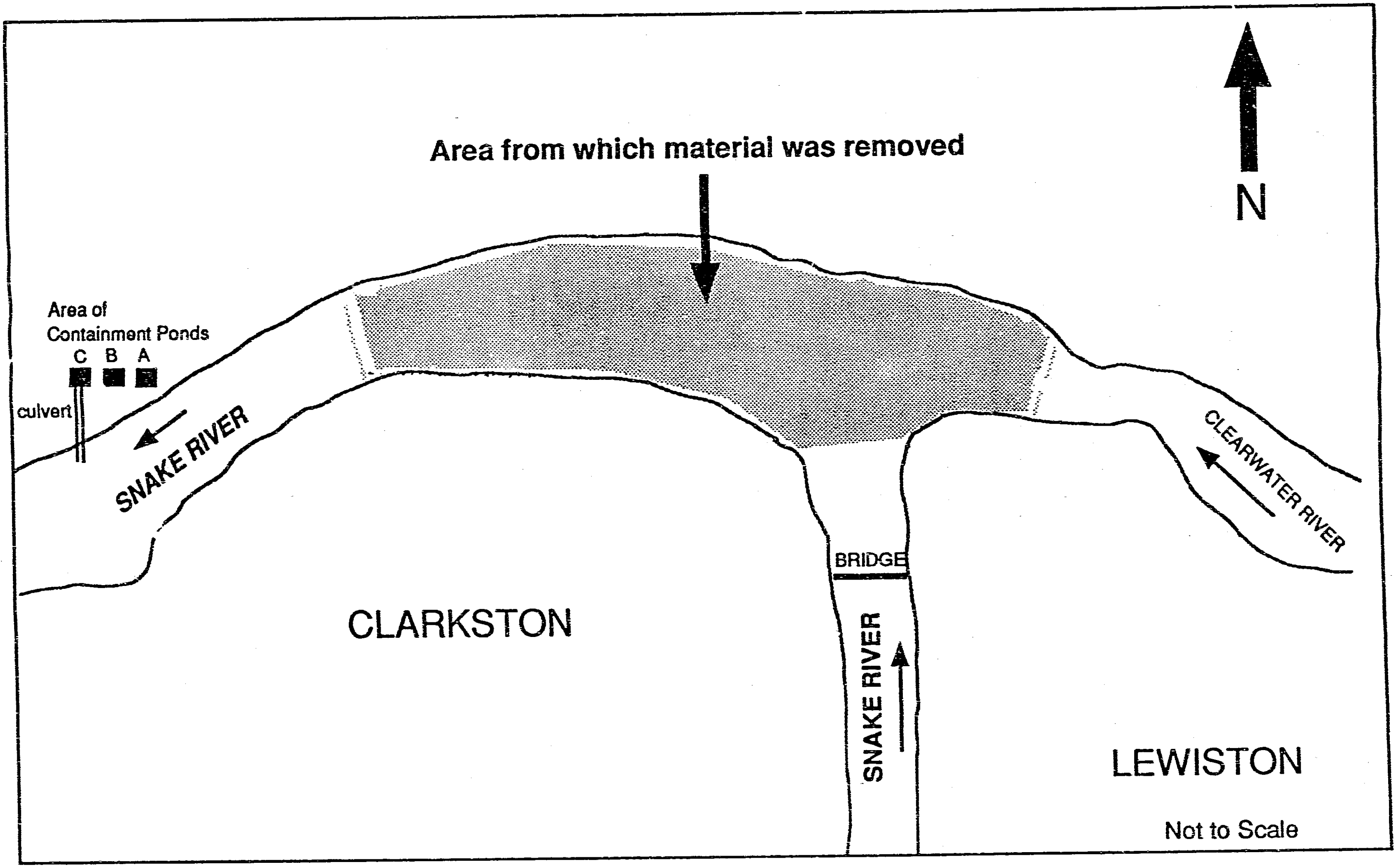

FIGURE 1.1. Study Area and Location of Containment Ponds

evaluations. The water-insoluble characteristics of dioxins and furans and their high affinity for organic material suggest that these compounds are most likely associated with fine particles, high in organic matter.

To determine possible dioxin and furan contamination, the USACE, Walla Walla District, and Waterways Experiment Station in Vicksburg, Mississippi, in conjunction with MSL personnel, designed the field sampling plan. Although dredged material was placed in ponds A and B, the study area focused on ponds B and C, areas containing fine-grained sediment, which had the greatest potential for dioxin contamination. A grid was set up on Pond C and the lower portion of Pond B consisting of 37 sampling stations. Once in the field, the USACE representative and MSL personnel decided to take two additional samples at grid 16. This was done because of a natural trench that cut through this grid, which was a likely place for potential dioxin accumulation.

All samples were analyzed for grain size, total organic carbon (TOC), and total volatile solids (TVS). Based on the location within the pond (Figure 1.2), only nine stations (the stations nearest the culvert that drains into the Snake River) were to be analyzed for dioxins and furans. Dioxin analysis included 2,3,7,8-TCDD at detection levels of 1 pptr and all other toxic dioxin and furan congeners to the lowest possible detection limit obtainable by the modified Environmental Protection Agency (EPA) Method 8290 (EPA 1986).

This report is divided into four sections. Section 2.0 presents the methods for sample collection, sample handling and processing, geologic observations, biological tests, physical and chemical analyses, and data analysis, as well as the quality assurance/quality control (QA/QC) considerations associated with each of these measurements. Results of geologic observations, sediment chemistry, toxicity tests, and bioaccumulation are given in Section 3.0. References are given in Section 4.0.

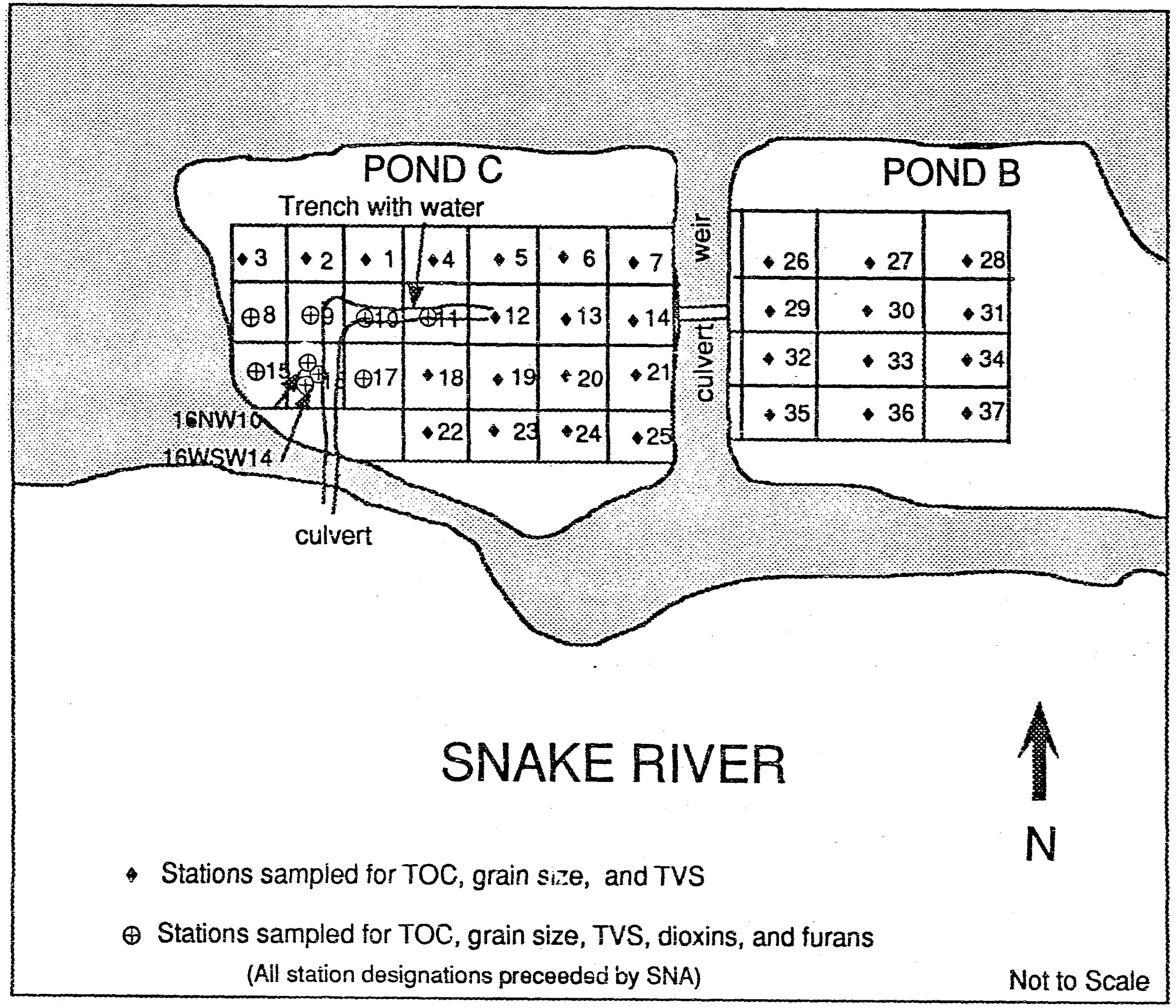

FIGURE 1.2. Locations of 39 Sampling Stations Within Containment Ponds B and C

2.0 METHODS

2.1 FIELD SAMPLING

The field sampling plan was designed jointly by a USACE representative and MSL personnel. Thirty-nine samples were taken and maintained at 4°C until subsampled for analyses. Samples were collected in the center of each of the 37 grids with the exception of grid 16, which was also sampled 10 ft to the northwest of the center (16 NW10), and 14 ft to the southwest (16 WSW14) of the center (Figure 1.2). The grids were set up by MSL based on pond topography and the presence of dredged sediment deposits. The northern edge of the pond was not sampled because it was devoid of dredged sediment deposits; consequently, the northern edge of the grid was moved south approximately 200 ft. Pond C comprised lush vegetation and wildlife (trees larger than 20 ft in height, cattails, nettles, beavers, etc), a trench filled with up to 2 ft of overlying water that intersected grids 9, 10, 11, and 16, and berms running north-south across grids 1, 2, 8, 9, 15, and 16. Based on the topography, grids were positioned in the following manner: the center of grids 2, 9, and 16 were positioned parallel to the west edge of the culvert (in a north-south line). The five grid lines running east and west were constructed parallel to each other and 100 ft apart. The eight grid lines running north-south were constructed parallel to each other and 50 ft apart. This scheme ensured that the stakes were positioned on the sampling station in the center of each grid. The dimensions for each grid cell on Pond C were 100 ft by 50 ft.

The sampling scheme for Pond B remained unchanged from the original design. Pond B contained much less vegetation than Pond C with low-growing grass, thistle, and dandelions. On the north side of the culvert under the berm between ponds B and C, dry cracks were noted to a depth of 27 in. and overlying water was not present at any of the 12 stations in Pond B. Grid lines for stations 26, 29, 32, and 35 were positioned parallel to and 15 ft from the edge of the berm. This area contained more silt and showed more distinct layering and sediment stratification than stations farther from the berm. The remaining eight stations were positioned in the north-south and east-west directions from the 26, 29, 32, and 35 grid lines (grid cell dimensions were 100 ft by 100 ft).

Stations containing overlying water were sampled using a 2-in. buterate core, which provided a sediment profile showing a definite layer of dredged material. After the core was collected, its contents were placed on a tray lined with clean aluminum foil. Sediment samples were taken from the deposited dredge materials using a stainless-steel spoon. Stations that did not have overlying water were sampled to the full depth of dredged material using a stainless-steel shovel. Material not in direct contact with the stainless-steel shovel was placed in pre-cleaned containers and included for sediment analyses. All samples were handled using clean Latex gloves. Samples were placed in EPA-approved, pre-cleaned, 1-gal glass containers. Samples were then stored at 4°C to maintain their original integrity.

Equipment used in the field was thoroughly rinsed after each sample collection using deionized water and acetone. Waste generated from this process was placed in a 5-gal bucket and secured with a lid. Equipment used in the laboratory was cleaned in the following manner: glassware was soap washed, rinsed with deionized water, soaked in 5% nitric acid for 4 h, and solvent rinsed with methylene chloride prior to use; stainless steel was soap washed and then rinsed with deionized water and methylene chloride.

Field observations included sampling station, date, time collected, sampling depth, physical characteristics of the sediment, and approximate location of each station (Table 2.1). A field chain-of-custody form was prepared listing all the collected samples and accompanied the samples to the MSL.

2.2 COMPOSITING OF SAMPLES FOR CHEMICAL ANALYSIS

Upon arrival at MSL, chemistry samples were inventoried against the chain-of-custody form and inspected for damage that may have occurred during shipping. After inspection, the samples were maintained at 4°C until used for compositing.

The compositing scheme involved mixing the contents of each sample to a homogeneous consistency. Subsamples for analyses included TOC, TVS, grain size, and dioxins. Three extra dioxin samples were taken at grid numbers 11, 16 WSW14, and 16 NW10. These extra samples were taken because their locations were in the direct path of a natural trench transecting Pond C, a potential area of fine sediment deposition.

Dioxin, TOC, TVS, and grain size samples were collected in I-Chem glass containers certified for EPA programs. Dioxins (16-oz glass containers) and grain size (4-oz plastic containers) samples were stored at 4°C until analyzed. The TOC (8-oz glass containers)

TABLE 2.1. Field Sampling Information for the 39 Stations

Sampling Station	Date	Sampling Equipment	Sediment Collected	Comments
Pond C				
SNA-1	4/24/91	shovel	1 gal	---
SNA-2	4/24/91	shovel	1 gal	top 2-in. darker soil above striations between dark and light brown
SNA-3	4/24/91	shovel	1 gal	top 2 to 4 in. matted with roots followed by a 2-in. silt layer sitting on 2 in. of firm sandy clay
SNA-4	4/24/91	shovel	1 gal	top 3 in. silt followed by 3 to 5 in. of sand
SNA-5	4/24/91	shovel	1 gal	top 2 in. silt followed by 5 in. sand
SNA-6	4/24/91	shovel	1 gal	sand to a depth of 10 in.
SNA-7	4/24/91	shovel	1 gal	sand from 2 to 7 in.
SNA-8	4/24/91	shovel	1 gal	soil appears entirely terrestrial, brown in color
SNA-9	4/24/91	2-in. core	1 gal	12 in. of light gray firm sand/clay over 10 in. of dark softer sediment
SNA-10	4/24/91	2-in. core	1 gal	4 in. standing water, 6 to 7 in. firmer sandy clay, gray followed by 12 in. soft material
SNA-11	4/24/91	2-in. core	1 gal	overlying water, 3 in. sand over 3 in. woody debris over sand
SNA-12	4/24/91	shovel	1 gal	top 2 in. dark brown silty material, woody debris layer at a depth of 11 in.
SNA-13	4/24/91	shovel	1 gal	sand to 12 in.
SNA-14	4/24/91	shovel	1 gal	vegetation on top followed by 12 in. of sand
SNA-15	4/24/91	shovel	1 gal	station appears terrestrial
SNA-16	4/24/91	2-in. core	1 gal	13 in. soft sediment lies over 5 in. firm sand
SNA-16 NW10	4/24/91	shovel	1 gal	fine silt and dredged material appeared to be mixed with bottom material from Ponds A and B which was deposited in Pond C.
SNA-16 WSW14	4/24/91	shovel	1 gal	2-in. layer of darker brown-gray material lies over firm brown sediment striations, roots and plant material present
SNA-17	4/24/91	shovel	1 gal	sand/silt striations sample taken to 1" on either side
SNA-18	4/24/91	shovel	1 gal	---
SNA-19	4/24/91	shovel	1 gal	silt from 2 to 7 in., then sand

TABLE 2.1. (contd)

Sampling Station	Date	Sampling Equipment	Sediment Collected	Comments
SNA-20	4/24/91	shovel	1 gal	sand present to 16-in. sample contained sand only
SNA-21	4/24/91	shovel	1 gal	sand begins 3 in. down
SNA-22	4/24/91	shovel	1 gal	2 in. of silt followed by 6 in. of sand
SNA-23	4/24/91	shovel	1 gal	thicker layer of silt from 2 to 8 in., then sand
SNA-24	4/24/91	shovel	1 gal	dry cracks, sand and silt at a depth of 3 in., sampled from 3 to 12 in.
SNA-25	4/24/91	shovel	1 gal	layers of sand and woodchips from 2 to 12 in.
Pond B				
SNA-26	4/25/91	shovel	1 gal	---
SNA-27	4/25/91	shovel	1 gal	---
SNA-28	4/25/91	shovel	1 gal	---
SNA-29	4/25/91	shovel	1 gal	---
SNA-30	4/25/91	shovel	1 gal	---
SNA-31	4/25/91	shovel	1 gal	---
SNA-32	4/25/91	shovel	1 gal	---
SNA-33	4/25/91	shovel	1 gal	---
SNA-34	4/25/91	shovel	1 gal	---
SNA-35	4/25/91	shovel	1 gal	---
SNA-36	4/25/91	shovel	1 gal	---
SNA-37	4/25/91	shovel	1 gal	---

samples were freeze-dried before analysis. Archived samples were maintained in 16-oz, pre-cleaned containers in the event that further analysis was required.

2.3 ANALYTICAL METHODS

The following briefly describes the methods used for analysis of sediment. Samples from 39 stations were submitted for selected analyses. Sediments were analyzed for TOC at Global Geochem in Canoga Park, California, TVSs at the MSL in Sequim, Washington, and grain size fractions were measured at Soil Technologies on Bainbridge Island, Washington. Nine of these samples were analyzed for 21 congeners of dioxins and furans at Twin City Testing in St. Paul, Minnesota.

2.3.1 Grain Size

Grain size of sediment samples was determined for four fractions (gravel, sand, silt, and clay) following the Puget Sound Estuary Program (PSEP) Protocols for Measuring Selected Environmental Variables in Puget Sound (PSEP 1986). These methods were consistent with ASTM D421 (ASTM 1978) and D422 (ASTM 1972).

Approximately 25 g of sediment were removed for analysis of total solids, while another 10- to 100-g aliquot was removed and weighed for grain size analysis. To separate the coarser sand and gravel fraction from the silt/clay fraction, sediment was washed with distilled water through a 63.5-µm (4.0-phi) sieve into a 1-L graduated cylinder. The coarse fraction was dried, weighed, and shaken through a nested series of sieves to yield the required seven coarse subfractions. Material still passing the final 63.5-µm sieve was added to the fine sediment previously collected in the graduated cylinder to determine the silt /clay fraction.

The silt/clay fraction was then subdivided by the pipet technique based on Stoke's Law of differential settling velocities for different-sized particles. The silt/clay fraction was disassociated by a dispersant in distilled water in a 1-L graduated cylinder. At specified time intervals and specified depths below the surface, 20-mL aliquots of suspension were withdrawn from the graduated cylinder, delivered to a preweighed container, and dried to constant weight at 90°±2°C.

Results were reported as a percentage of gravel, sand, silt, and clay. Quality assurance measures included duplicate analysis of sample SNA-24. Matrix spikes, standard reference materials (SRM), and detection limits do not apply to grain size.

2.3.2 Total Organic Carbon

The TOC in sediment was determined by measuring the carbon dioxide released during combustion of the sample (PSEP 1986; SW846 Method 9060, EPA 1986) and included the amount of non-volatile, partially volatile, volatile, and particulate organic compounds in a sample. This process involved drying and ball milling the sample to a fine powder, and before combustion, removing the inorganic carbonate by acidification.

Results were reported as percent of dry weight. Quality assurance measures included triplicate analysis on SNA-16 WSW14. To further ensure precision, duplicate analyses were run on samples SNA-1, SNA-10, SNA-20, and SNA-30. The SRM MESS-I was also included for quality assurance.

2.3.3 Total Volatile Solids

Total volatile solids measure the fraction of total solids lost on ignition and are an estimate of the amount of organic matter in the total solids. Analyses of TVS followed the method defined in PSEP (1986). The sample was first freeze-dried to a constant weight and ball milled to a fine powder. Then, a portion of the sample was removed, weighed, and combusted at 550°C. This portion was cooled in a desiccator and reweighed. The amount of sample lost during ignition was then defined as the volatile solids fraction.

Two analytical blanks and two sample duplicates (SNA-16 WSW14 and SNA-37) were analyzed for quality assurance measures.

2.3.4 Chlorinated Dioxins and Furans

The following is a list of abbreviations for chlorinated dioxins and furans:

Abbreviation	Chlorinated compound
OCDD	Octachlorodibenzodioxin
OCDF	Octachlorodibenzofuran
HpCDD	Heptachlorodibenzodioxin
HpCDF	Heptachlorodibenzofuran
HxCDD	Hexachlorodibenzodioxin
HxCDF	Hexachlorodibenzofuran
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PCDPE	Polychlorinated diphenylether
PeCDD	Pentachlorodibenzodioxin

PeCDF	Pentachlorodibenzofuran
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran

Nine sediment samples from the Wilma Uplands disposal site (Pond C) were analyzed for 21 congeners of PCDDs and PCDFs using a modified EPA Method 8290 (EPA 1986). This method, referred to as an isotope dilution method, involves spiking each isotope or compound of interest prior to extraction. A number of modifications to the draft version of EPA Method 8290 were used in dioxin analyses and were primarily drawn from the more recent EPA Method 1613. One modification involved substituting the calibration and spiking standards described in Method 1613 for those described in Method 8290. This modification expanded the calibration range and introduced additional isotopically labelled standards that improve the accuracy of the quantifications. The analyte enrichment process also contained modifications from Method 1613 and included changes to column preparation and elution. Other modifications included as standard operating procedures were the use of 1-µL injections.

Sediment aliquots were subsampled and spiked with isotopically labelled internal standards and continuously extracted for 18 h with benzene in a soxhlet extraction apparatus. Extracts were then reduced and exchanged into hexane using a Kuderna-Danish concentrator. These hexane extracts were "cleaned" to remove interfering matrices and spiked with an enrichment efficiency standard (^{37}Cl-2,3,7,8-TCDD) prior to the enrichment process. This was followed by an analyte enrichment process that involved liquid chromatography of the extract through acidified silica gel and sodium hydroxide.

After the silica gel cleanup, the extracts were reduced again to 1 mL and fractionated on a variety of columns, including alumina and activated carbon, and eluted with various solvents to isolate the compounds of interest. The final extracts were transferred back to hexane and spiked with the two recovery standards (1,2,3,4-TCDD-$^{13}C_{12}$ and 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$).

These extracts were analyzed for the presence of PCDDs and PCDFs using a combined capillary column gas chromatography/high resolution mass spectrometry (GC/HRMS). This resolution was sufficient to resolve most interferences, thus assuring the detected levels of PCDD and PCDF were not related to interferences. The PCDD and PCDF isomers were quantified by comparison of their responses to the responses of the labelled internal standards. Relative response factors were calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels and each of the internal standards at one concentration level. The detection limit was based on producing a signal that was 2.5 times the noise level and was calculated for each 2,3,7,8-substituted isomer of any tetra- through octa-chlorinated congener class. The noise heights used to calculate the detection limits were measured at the retention time of the specific isomer.

Extraction efficiency and enrichment efficiency were determined by comparing the recovery of the enrichment efficiency standard (^{37}Cl-2,3,7,8-TCDD) and the $^{13}C_{12}$ labelled internal standard relative to one of the recovery standards ($^{13}C_{12}$ and 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$).

Quality assurance measures included duplicate analysis of sample SNA-15 and blank and blank spike percent recovery to measure both accuracy and precision. Results of dioxins and furans were reported as ng/kg dry weight.

3.0 RESULTS

Quality assurance measures used in this study include matrix spikes, which assess accuracy (percent recovery), spike and spike duplicates and analytical replicates, which assess precision [relative percent difference (RPD) and relative standard deviation (RSD)], and method blanks, which assess potential contamination of samples. The results of each chemical analysis are followed by a quality assurance statement and are described below and presented in Tables 3.1 through 3.9.

3.1 GRAIN SIZE

Thirty-nine samples were analyzed for four fractions of grain size. Results of sediment grain size analysis, presented in Tables 3.1 and 3.2, were determined for the four fractions (gravel, sand, silt, and clay). Twenty-eight stations contained fine silty material, ranging from 0.0039 mm to 0.0625 mm. Eleven stations contained sediments that were predominantly sand sized or larger, ranging from 0.063 mm to 2.00 mm. Two stations, SNA-7 and SNA-15, had approximately equal portions of sand/silt.

The accuracy of the analysis was determined by calculating the RPD between sample duplicates. Two samples, SNA-4 and SNA-24, were analyzed in duplicate to determine the precision of the measurement. Relative percent differences between duplicate analyses ranged from 1.71% to 3.28%, indicating acceptable precision of the method. Matrix spikes and SRMs do not apply to grain size analyses.

3.2 TOTAL ORGANIC CARBON

Total organic carbon was measured on 39 sediment samples and reported in Tables 3.3 and 3.4 as percent dry weight. The results ranged from 0.17% at SNA-14 to 3.55% at SNA-25. The higher levels of TOC at SNA-7, SNA-11, SNA-12, SNA-20, SNA-24, SNA-25, SNA-26, SNA-32, and SNA-35 are probably attributable to the fine-grained nature of these sediments (Table 3.1) and the presence of root material within the samples from those sites. Five samples were analyzed in duplicate (SNA-1, SNA-10, SNA-20, SNA-30, and SNA-37) to assess precision. The RPD ranged from 1.19% to 3.77%. To further assure precision, one sample was analyzed in triplicate (SNA-16 WSW14) with a RSD of 1.59%. The RPDs and RSDs calculated

TABLE 3.1. Grain Size Results for Wilma Uplands Disposal Site

Sampling Station	% Total Solids	Percent Dry Weight in Each Size Fraction			
		% Gravel ≥2.00 mm	% Sand 0.063-2.00 mm	% Silt 0.0039-0.0625 mm	% Clay ≤0.0039 mm
SNA-1	78.25	1	27	62	10
SNA-2	67.63	0	12	69	19
SNA-3	65.73	0	25	66	9
SNA-4	72.52	0	31	54	15
SNA-4 dup	72.52	0	32	53	15
SNA-5	63.50	0	17	62	21
SNA-6	72.46	0	35	60	5
SNA-7	75.93	0	44	48	8
SNA-8	77.92	2	34	56	8
SNA-9	61.55	0	27	57	16
SNA-10	57.59	0	15	64	21
SNA-11	43.64	1	17	63	19
SNA-12	59.47	0	21	62	17
SNA-13	77.63	0	37	52	11
SNA-14	66.36	0	19	67	14
SNA-15	78.48	9	41	40	10
SNA-16	63.58	0	28	58	14
SNA-16 NW10	74.68	0	24	62	14
SNA-16 WSW14	65.64	0	13	64	23
SNA-17	68.75	0	15	64	21
SNA-18	69.76	0	30	55	15
SNA-19	66.17	0	26	56	18
SNA-20	67.52	0	39	52	9
SNA-21	84.45	0	66	29	5
SNA-22	63.72	0	19	58	23
SNA-23	67.47	0	23	58	19
SNA-24	59.95	0	31	58	11
SNA-24 dup	59.95	0	30	59	11
SNA-25	63.57	0	52	44	4
SNA-26	75.27	0	37	55	8
SNA-27	83.81	0	58	35	7
SNA-28	88.61	0	86	11	3
SNA-29	87.34	1	58	36	5
SNA-30	93.58	0	91	7	2
SNA-31	92.53	0	94	5	1
SNA-32	79.55	0	30	60	10
SNA-33	89.75	0	89	9	2
SNA-34	94.53	0	94	5	1
SNA-35	73.61	0	30	59	11
SNA-36	89.98	0	74	22	4
SNA-37	93.80	0	90	8	2

TABLE 3.2. Quality Assurance Data for Grain Size Analysis of Wilma Uplands Disposal Site

Sampling Station	Percent Dry Weight in Each Size Fraction % Total Solids	% Gravel ≥2.00 mm	% Sand 0.063-2.00 mm	% Silt 0.0039-0.0625 mm	% Clay ≤.0039 mm
SNA-4	72.52	0.00	31.00	54.00	15.00
SNA-4 dup	72.52	0.00	32.00	53.00	15.00
RPD	0.00	0.00	3.17	1.87	0.00
I-Stat	0.00	0.00	0.02	0.01	0.00
SNA-24	59.95	0.00	31.00	58.00	11.00
SNA-24 dup	59.95	0.00	30.00	59.00	11.00
RPD	0.00	0.00	3.28	1.71	0.00
I-Stat	0.00	0.00	0.02	0.01	0.00

for the duplicate and triplicate measurements are within the quality assurance/quality control (QA/QC) guideline of ±10% set for precision. One SRM (sample MESS-1) was measured during the analysis to assess accuracy of the method. Although this sample is not certified for TOC, frequent analysis of this sample at the MSL has established a TOC concentration of approximately 2.2%. This value agrees with the measured values of 2.33% and 2.32% determined for this analysis.

3.3 TOTAL VOLATILE SOLIDS

Total volatile solids were measured in 39 samples from the Wilma Uplands Disposal Site. Results for TVS (percent dry weight) are presented in Tables 3.5 and 3.6. The TVS concentrations ranged from 1.28% at SNA-31 to 8.94% at SNA-25. The general pattern is such that those stations having the highest TOC values also had the highest TVS values (SNA-7, SNA-11, SNA-12, SNA-20, SNA-24, SNA-25, SNA-26, SNA-32, and SNA-35).

The precision of the analysis was evaluated with two samples analyzed in duplicate (SNA-37 and SNA-16 WSW14). The RPD among duplicate samples ranged from 1.19% to 1.40%, indicating acceptable precision for this method. Two blanks were analyzed with the samples and showed no measurable levels of TVS.

TABLE 3.6. Total Organic Carbon Results for the Wilma Uplands Disposal Site

Sampling Station	TOC (percent dry weight)
SNA-1	0.28
SNA-1 dup	0.28
SNA-2	0.72
SNA-3	0.23
SNA-4	0.54
SNA-5	1.44
SNA-6	1.66
SNA-7	3.06
SNA-8	0.34
SNA-9	0.92
SNA-10	1.52
SNA-10 dup	1.49
SNA-11	2.92
SNA-12	2.85
SNA-13	1.64
SNA-14	0.17
SNA-15	0.56
SNA-16	0.46
SNA-16 NW10	0.37
SNA-16 WSW14 Rep 1	0.96
SNA-16 WSW14 Rep 2	0.98
SNA-16 WSW14 Rep 2	0.95
SNA-17	0.57
SNA-18	1.11
SNA-19	1.38
SNA-20	2.50
SNA-20 dup	2.53
SNA-21	0.37
SNA-22	1.83
SNA-23	1.28
SNA-24	2.80
SNA-25	3.55
SNA-26	2.31
SNA-27	1.72
SNA-28	0.26
SNA-29	1.74
SNA-30 dup	0.19
SNA-30	0.19
SNA-31	0.24
SNA-32	2.76
SNA-33	0.30
SNA-34	0.27
SNA-35	2.11
SNA-36	0.73
SNA-37	0.27
SNA-37 dup	0.26

TABLE 3.4. Quality Assurance Data for Total Organic Carbon Analysis of Wilma Uplands Disposal Site

Sampling Station	TOC (percent dry weight)
Analytical Duplicates	
SNA-1	0.28
SNA-1 dup	0.28
RPD	0.00
I-Stat	0.00
SNA-10	1.52
SNA-10 dup	1.49
RPD	1.99
I-Stat	0.01
SNA-20	2.50
SNA-20 dup	2.53
RPD	1.19
I-Stat	0.01
SNA-30	0.19
SNA-30 dup	0.19
RPD	0.00
I-Stat	0.00
SNA-37	0.27
SNA-37 dup	0.26
RPD	3.77
I-Stat	0.02
Analytical Triplicates	
SNA-16 WSW14 Rep 1	0.96
SNA-16 WSW14 Rep 2	0.98
SNA-16 WSW14 Rep 3	0.95
RSD	1.59
Standard Reference Material	
MESS-1 Rep 1	2.33
MESS-1 Rep 2	2.32
MSL established value	2.20

TABLE 3.5. Total Volatile Solids Results for Wilma Uplands Disposal Site

Sampling Station	TVS (percent dry weight)
SNA-1	3.02
SNA-2	4.35
SNA-3	3.56
SNA-4	3.24
SNA-5	5.66
SNA-6	5.48
SNA-7	8.86
SNA-8	3.18
SNA-9	4.81
SNA-10	6.22
SNA-11	8.87
SNA-12	8.82
SNA-13	5.73
SNA-14	3.73
SNA-15	4.01
SNA-16	4.19
SNA-16 NW10	3.49
SNA-16 WSW14	5.03
SNA-16 WSW14 dup	5.09
SNA-17	4.41
SNA-18	4.84
SNA-19	5.92
SNA-20	7.94
SNA-21	1.88
SNA-22	6.11
SNA-23	4.78
SNA-24	7.48
SNA-25	8.94
SNA-26	7.00
SNA-27	5.37
SNA-28	1.30
SNA-29	5.47
SNA-30	1.29
SNA-31	1.28
SNA-32	8.31
SNA-33	1.58
SNA-34	1.33
SNA-35	6.74
SNA-36	2.74
SNA-37	1.44
SNA-37 dup	1.42

TABLE 3.6. Quality Assurance Data for Total Volatile Solids Analysis of Wilma Uplands Disposal Site

Sampling Station	TVS (percent dry weight)
Analytical Blanks	
Blank 1	0.06
Blank 2	0.06
Sample Duplicates	
SNA-37	1.44
SNA-37	1.42
RPD	1.40
I-Stat	0.01
SNA-16 WSW14	5.03
SNA-16 WSW14	5.09
RPD	1.19
I-Stat	0.01

3.4 CHLORINATED DIOXINS AND FURANS

Chlorinated dioxins and furans were measured in nine sediment samples from the Wilma Uplands Disposal Site (Table 3.7). Results of dioxin and furan analyses are presented in Tables 3.7 through 3.9 and are reported as pptr. Chemical analysis of the nine samples resulted in undetected (U) concentrations of 2,3,7,8-TCDD/TCDF ranging from 0.37 (U) to 1.70 (U) pptr. Chlorinated congeners of dioxins were detected in some of the stations ranging from 0.15 pptr (12378-PeCDD) at SNA-16WSW14 to 95 pptr (OCDD) at Station SNA-11. Chlorinated congeners of furans were also detected in some stations, ranging from 0.20 pptr at SNA-15 dup (1234678-HpCDF) to 7.20 pptr (OCDF) at SNA-11.

Quality assurance measures for dioxin and furan analysis consisted of internal standards, efficiency standards, method blanks, and blank spikes. The internal standards were used to quantify corresponding dioxin analytes that were added prior to the extraction process and to assess all processes involved in the method (i.e., extraction, enrichment, and analytical performance). Prior to enrichment, the enrichment efficiency standard was added to the samples after extraction to assess the clean-up procedure only. The range of acceptable

TABLE 3.7. Results of Dioxin/Furan Analysis for Sediments from the Wilma Uplands Disposal Site

Method Analyte	Sampling Station (concentration in pptr dry weight) SNA-8	SNA-9	SNA-10	SNA-11	SNA-15	SNA-15 DUP	SNA-16	SNA-17	SNA-16 NW10	SNA-16 WSW14
Chlorinated Dioxins										
2378-TCDD	0.48U[a]	1.40U	1.20U	1.60U	0.73U	0.84U	0.50U	0.45U	0.37U	1.70U
Total TCDD	ND[b]	ND	1.00	ND	ND	ND	ND	ND	0.43	ND
12378-PeCDD	0.24U	0.35U	0.60U	0.30U	0.10U	0.16U	0.25U	0.16U	0.14U	0.15
Total PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
123478-HxCDD	0.28U	1.10U	0.44U	0.21U	0.37U	0.41U	0.17U	0.17U	0.06U	0.27U
123678-HxCDD	0.26U	0.77U	0.39	0.56U	0.31U	0.19U	0.22	0.18	0.14U	0.59
123789-HxCDD	0.31U	1.10U	0.54U	0.73U	0.44U	0.14U	0.45U	0.33U	0.19U	0.93U
Total HxCDD	ND	1.10	1.80	5.20	ND	ND	0.97	0.67	0.46	3.00
1234678-HpCDD	1.20	6.80	10.00	14.00	2.40	1.60	4.00	3.90	1.00U	8.60
Total HpCDD	1.20	12.00	18.00	26.00	2.40	2.60	9.00	8.10	ND	16.00
OCDD	9.10	53.00	73.00	95.00	18.00	14.00	41.00	39.00	11.00	75.00
Chlorinated Furans										
2378-TCDF	0.63U	0.90U	1.00U	1.40U	1.70U	0.59U	0.38U	0.40U	0.29U	1.50U
Total TCDF	ND	ND	ND	0.77	ND	ND	ND	ND	ND	ND
12378-PeCDF	0.41U	0.41U	0.40U	0.32U	0.40U	0.25U	0.15U	0.14U	0.11U	0.53U
23478-PeCDF	0.27U	0.44U	0.25U	0.32U	0.16U	0.20U	0.20U	0.16U	0.09U	0.31U
Total PeCDF	ND	ND	ND	ND	ND	ND	ND	ND	0.32	0.47

TABLE 3.7. (contd)

Method Analyte	Sampling Station (concentration in pptr dry weight) SNA-8	SNA-9	SNA-10	SNA-11	SNA-15	SNA-15 DUP	SNA-16	SNA-17	SNA-16 NW10	SNA-16 WSW14
123478-HxCDF	0.27U	0.41U	0.45U	0.64U	0.24U	0.17U	0.12U	0.17U	0.10U	0.42U
123678-HxCDF	0.23U	0.32U	0.41U	0.52	0.22U	0.23U	0.19U	0.11U	0.05U	0.41U
123789-HxCDF	0.42	0.72U	0.49	0.69	0.28	0.39	0.61	0.58	0.35U	0.49U
234678-HxCDF	0.20U	0.50U	0.31U	0.32U	0.10U	0.19U	0.15U	0.13U	0.13U	0.37U
Total HxCDF	0.42	0.56	1.30	2.40	0.28	0.39	1.20	0.79	ND	0.55
1234678-HpCDF	0.41U	1.20	2.10	2.30	0.49U	0.20	1.10	0.83U	0.22U	1.60
1234789-HpCDF	0.17U	0.56U	1.10U	0.29U	0.26U	0.19U	0.13U	0.19U	0.08U	0.43U
Total HpCDF	ND	1.20	5.70	6.60	0.51	0.64	2.10	1.20	ND	4.30
OCDF	0.52	3.90	4.80	7.20	0.98	0.82	2.60	2.60	0.58	5.50

(a) U Analyte was not present above the level of associated value.
(b) ND Not detected.

TABLE 3.8. Quality Assurance Data for Dioxins/Furans From Sediments Within the Wilma Uplands Disposal Site

Method Analyte	Sampling Station (concentration in pptr dry weight)											
	SNA-8	SNA-9	SNA-10	SNA-11	SNA-15	SNA-15 DUP	SNA-16	SNA-17	SNA-16 NW10	SNA-16 WSW14	Blank	Blank Spike
INTERNAL STANDARDS												
2378-TCDD-C13	72	59	66	61	37	46	59	56	67	65	52	38
12378-PeCDD-C13	85	73	87	86	66	67	68	65	83	84	90	71
123478-HxCDD-C13	84	68	80	73	65	65	70	67	81	74	82	76
123678-HxCDD-C13	74	63	70	64	53	63	61	59	90	60	81	58
1234678-HpCDD-C13	123	100	108	99	73	110	62	63	96	92	132	109
OCDD-C13	96	68	87	85	61	71	51	58	86	75	101	90
2378-TCDF-C13	62	52	58	53	30	38	49	53	59	56	40	30
12378-PeCDF-C13	71	64	78	77	54	58	59	57	73	69	72	52
23478-PeCDF-C13	71	63	76	73	57	54	65	64	81	69	81	61
123478-HxCDF-C13	83	70	76	63	50	62	55	59	93	70	80	62
123678-HxCDF-C13	67	58	64	57	47	54	54	57	86	57	68	59
123789-HxCDF-C13	66	56	63	55	47	52	63	57	86	54	69	58
234678-HxCDF-C13	96	78	85	74	61	75	68	62	83	74	97	78
1234678-HpCDF-C13	94	73	74	76	52	71	62	59	87	68	93	76
1234789-HpCDF-C13	102	85	91	92	61	81	63	66	95	81	110	90
ENRICHMENT EFFICIENCY STANDARD												
2378-TCDD-C137	72	55	63	54	46	46	61	54	64	59	46	36

TABLE 3.9. Quality Assurance Data for Blank Spike Recoveries

Method Analyte	Blank (pptr)	Spiked (ng)	Recovered (ng)	% Recovery
2378-TCDD	1.20U[a]	0.2	0.16	80
Total TCDD	ND[b]	0.2	0.16	80
12378-PeCDD	0.28U	1.0	0.75	75
Total PeCDD	ND	1.0	0.75	75
123478-HxCDD	0.20U	1.0	0.70	70
123678-HxCDD	0.24U	1.0	0.94	94
123789-HxCDD	0.31U	1.0	0.94	94
Total HxCDD	ND	3.0	2.6	87
1234678-HpCDD	0.69U	1.0	0.75	75
Total HpCDD	ND	1.0	0.75	75
OCDD	6.90	2.0	1.4	70
2378-TCDF	1.30U	2.0	0.17	85
Total TCDF	ND	2.0	0.17	85
12378-PeCDF	0.17U	1.0	0.75	75
23478-PeCDF	0.16U	1.0	0.76	76
Total PeCDF	ND	2.0	1.5	75
123478-HxCDF	0.22U	1.0	0.79	79
123678-HxCDF	0.45U	1.0	0.71	71
123789-HxCDF	0.36U	1.0	0.74	74
234678-HxCDF	0.32U	1.0	0.76	76
Total HxCDF	ND	4.0	3.0	75
1234678-HpCDF	0.46U	1.0	0.77	77
1234789-HpCDF	0.55U	1.0	0.82	82
Total HpCDF	ND	2.0	1.6	80
OCDF	0.54	2.0	1.5	75

(a) U Analyte was not present above the level of associated value.
(b) ND Not detected.

recoveries for standards as stated in the QA Plan for this project was 40% to 120%. However, recoveries of internal standards above 25% are acceptable based on the EPA Method 1613 recommendation. Recoveries of the PCDD and PCDF internal standard of the native compounds ranged from 47% to 132% from the penta- through octa-chlorinated congener classes. Lower recoveries ranging from 30% to 72% were obtained for the tetra-chlorinated standards. The recoveries for the penta- through octa- series met acceptable requirements for both the project QA plan and the EPA criteria. The recoveries for the tetra-chlorinated series were slightly below the acceptable criteria for the QA plan, but within the acceptable range as established by EPA; therefore, no corrective action was necessary.

Lower recoveries for the tetra-chlorinated standards may be attributed to changes in the extraction laboratory such as humidity and temperature, which affect enrichment procedures and can parallel fluctuations in environmental conditions. However, because the dilution of these isotopic standards was used to quantify the native compounds, the data are automatically corrected from variations in recovery and accurate values are obtained.

The range of recovery for the enrichment efficiency standards was 36% in the blank spike to 72% in SNA-8. Again, this range is slightly below acceptable levels for the QA plan but within acceptable levels set forth by EPA for this method; therefore, no corrective action was necessary.

The results for the method blank analysis showed no evidence of PCDD and PCDF isomers, with the exception of low background levels of OCDF (0.54 pptr) and OCDD (96.9 pptr). However, these levels were below those of the actual test sediments, with the exceptions of SNA-8 and SNA-16 NW10 that contained OCDD and OCDF levels similar to the blank levels. The concentrations of OCDD and OCDF for these samples may be attributed to background interference.

A blank PCDD and PCDF spike sample was also prepared with the test samples by extracting clean sand fortified with native standard materials. The results show that the native compounds were recovered at levels ranging from 70% to 94%, which is within the acceptable range of 40% to 120% established in the QA plan, and indicates acceptable accuracy of the analysis.

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